

Relations Between High-Temperature Mastication and Mooney Viscosity Relaxation in Natural Rubber

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ABSTRACT: Mastication of natural rubber (NR) is undertaken as a preliminary step towards the preparation of NR-based vulcanizates, a process during which the elastomer is broken down to a homogeneous matrix of lower viscosity. Several tests and indicators are in use for characterizing the behavior of elastomers but these have mostly been adopted for the nonmasticated product. This study uses coefficients generated from modeled Mooney relaxation data, as indicators of elasticity, to examine the effect of high-temperature mastication on the processability of the masticated rubber. Some derived coefficients such as the terminal relaxation time (τ) from Maxwell's triexponential model, the elastic component (a) from Wu-Abbott model [$Y = 1 + a^* \ln(t) - bt/(c + t)$], and the constant (b)

from the Power law model ($Y = at^{-b}$), adequately characterized the effect of mastication on NR. Although the NR grades studied were quite different with respect to their initial molar mass distributions, they followed a similar response to the mechanical models before and after mastication, indicating therefore that mastication decomposes to a similar extent, the various components (long isoprene chains, densely crosslinked solvent-insoluble gel, etc.) that account for the viscoelastic behavior of the raw elastomer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2785–2790, 2009

Key words: natural rubber; polyisoprene; mastication; Mooney viscosity; relaxation; modeling

INTRODUCTION

Mastication, in the natural rubber (NR) industry, involves transforming the raw elastomer into a more uniform product of lower viscosity. In principle, the processability of the masticated elastomer conditions the efficiency with which other ingredients are incorporated within the rubber matrix.¹ Recent research on the mastication of NR has been dedicated to its effects on the elastomer's bulk properties^{2–4} and macromolecular structure,^{5,6} although some have nonetheless been directed to its effects on the processability of compounded stocks under different strain amplitudes,⁷ or using conventional test equipment (such as rotational and capillary viscometers)⁸ and nonconventional processability test equipment.⁹ Often, some of this equipment is criticized for their low strain rates (10 to 1 s⁻¹) when compared to strain rates in industrial processing equipment (10³ to 10⁴ s⁻¹).

The Mooney viscosity (ISO 289) is a steady low shear rate (≈ 1.6 s⁻¹) rotational viscosity test used to

characterize the processability of elastomers.^{10,11} Unlike other tests performed at low strain rates, this viscosity compares favorably with some high shear tests like the capillary rheometry,¹⁰ correlates well with NR's average molar mass and die swell,^{12,13} and is satisfactorily discriminant, especially at reduced rotor speeds.¹⁴ Furthermore, the Mooney viscosity decay (relaxation) could be modeled with suitable mechanical equations to generate coefficients that better characterize the structure and viscoelasticity of NR.¹⁵ This study evaluates the suitability of coefficients generated from the relaxation of the Mooney viscosity of masticated rubber for use in characterizing the processability of NR during high temperature mastication.

MATERIALS AND METHODS

Materials

The study was conducted on two NR grades (TSR3CV and TSR10) prepared with latex from a pool of about 150 *Hevea brasiliensis* trees (clone PR107).

To prepare grade TSR3CV rubber, fresh latex was collected from half of the trees, bulked, treated with 0.05% w/v ammonia solution (1 L for 100 L latex) to

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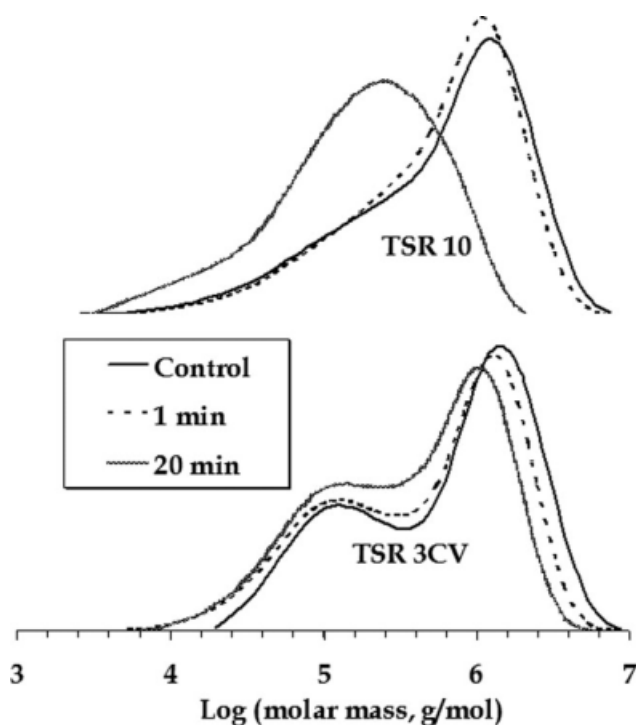


Figure 1 Initial molar mass distributions of the natural rubber samples of grade TSR 10 and grade TSR 3CV and their evolution during high-temperature mastication.

prevent premature coagulation, and stabilized with neutral hydroxylamine sulfate (0.8 g/kg dry rubber) to inhibit storage-hardening reactions.¹⁶ Formic acid was introduced into the whole (at 0.15% v/v latex) to provoke coagulation of rubber particles at pH 5. About 16 h later, the coagulum was crumbed, washed, dried (4 h at 115°C), and compacted. All solvents were of AnalaR grade (Labosi, Elancourt, France) unless indicated otherwise.

To prepare the TSR10 rubber, latex from the remaining half of the trees was left to coagulate naturally in collection cups, stored on barns under shade for 24 days to mature naturally, and the coagula were crumbed, washed, dried (5.5 h at 115°C), and compacted.

The Mooney viscosity (MS3+4) at 100°C, at production of the rubber grades, was 30 and 60 Mooney units for the TSR3CV and TSR10, respectively. Their molar mass distributions (MMDs) were equally different (Fig. 1). Initially, the MMD was unimodal and composed essentially of polyisoprene chains of very high molar mass entities (10^6 g/mol) for the TSR10 and bimodal with polyisoprene chains of very high (10^6 g/mol) and relatively low (10^5 g/mol) molar masses for the TSR3CV. These MMDs have been shown to evolve differently (Fig. 1) during high-temperature mastication¹⁷: progressive decrease in high molar mass chains and increase in low molar mass entities for the TSR10 rubber, and a rather less pro-

gressive decrease for the TSR 3CV rubber, and even stagnation on prolonged mastication of the latter.

Mastication of NR

Rubber samples were masticated in a 70-cm³ capacity internal mixer (Rheomix 600p, Haake Poly-lab) equipped with a central processing unit attached to a microcomputer, a motoring unit, and two rotors (557-1030 type rollers). Prior to mastication, the system was preheated and maintained at 120°C and the rotor speed set at 100 rpm. A 48-g rubber portion was inserted in the mastication chamber (75% fill factor) and masticated for varying durations. Due to viscous dissipation, gum temperatures increased considerably and remained well above 115°C after the first minute of mastication.¹⁷ At these high temperatures, rubber degradation that ensued was caused essentially by thermal oxidation.^{18–20}

Relaxation of the Mooney viscosity

Rubber test portions were cut into cylindrical test pieces (45-mm diameter, ~ 6 mm thick) and tested for their Mooney viscosity on a Mooney MkIII viscometer (H.W.Wallace, UK). Using the small rotor (30.48-mm diameter and 5.54-mm thick) at a test temperature of 100°C, the Mooney viscosity was determined after subjecting test portions to 3 min preheating and 4 min shearing (MS3+4 at 100°C). For most NR samples sheared in a Mooney viscometer, the torque increases rapidly to a maximum value (V_{max}), rapidly decreases thereafter to a minimum (V_{min}), and then increases slowly to a plateau or final value (V_R) after 2–4 min (Fig. 2). In the course of this study, the entire Mooney torque variation was transmitted as electrical signals from the viscometer's transducer, via an RS232 interface-equipped multimeter (VoltcraftME42) to a computer and recorded using the MScope[®] software.

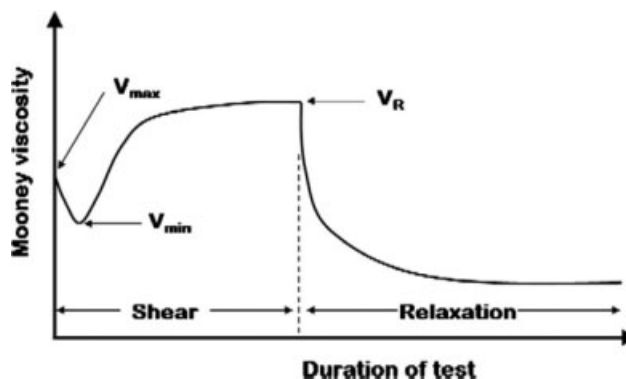


Figure 2 General profile of the evolution of the Mooney torque during shearing and relaxation in a Mooney viscometer.

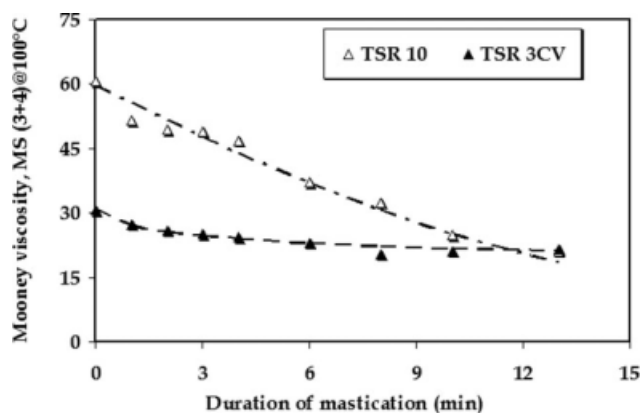


Figure 3 Effect of high-temperature internal mixer mastication on the Mooney viscosity of technically specified natural rubber of grades TSR10 and TSR3CV.

Modeling Mooney viscosity relaxation

Normalized Mooney torque relaxation values ($ML_N(t) = ML_t/ML_0$) were recorded over a time window of 500 s and modeled using the Datafit[®] version 8.0 software (Oakdale Engineering, 2002). The parameters $ML_N(t)$, ML_t , and ML_0 were the normalized torque, the torque value at time t , and the torque value when the rotor stopped ($t = 0$), respectively. Several mathematical models were evaluated and three of these, hitherto judged suitable for describing Mooney viscosity relaxation on nonmasticated NR, are presented here.¹⁵

The first evaluated equation [eq. (1)] was an empirical model proposed by Wu and Abbott²¹ for firmness relaxation on tomatoes and by Ehabe et al.¹⁵ for Mooney relaxation in nonmasticated NR

$$ML_N(t) = 1 - a \cdot \ln(1 + t) - \frac{b \cdot t}{c + t} \quad (1)$$

The coefficients of nonlinear regression, a and b , had been found to be proportional to the respective elastic and viscous components of the measure and describe the extent of relaxation and the overall viscoelasticity of the material.

The second evaluated model [eq. (2)] was a triexponential equation derived from Maxwell's constitutive model, where $a = ML_N(t)$ for $t \rightarrow \infty$, $b + d + g = ML_N(0)$, while the constants c , f , and h were relaxation times ($\tau_i = \eta_i/G_i$).

$$ML_N(t) = a + b \cdot \exp\left(-\frac{t}{c}\right) + d \cdot \exp\left(-\frac{t}{f}\right) + g \cdot \exp\left(-\frac{t}{h}\right) \quad (2)$$

From eq. (2), the effect of mastication on Mooney relaxation was characterized in terms of the terminal relaxation time ($\tau = c + f + h$).

The third model tested was the Power law equation [eq. (3)]. Although this model does not seem to adequately describe Mooney relaxation in nonmasticated NR,¹⁵ it was judged useful as it has often been recommended elsewhere when characterizing relaxation in masticated NR^{22,23} and in synthetic elastomers^{24,25}

$$ML_t = a \cdot t^{-b} \quad (3)$$

The nonlinear regression coefficient a is the power-law constant (Mooney torque 1 s after shearing ceases) and b is the power-law index characterizing the rate of relaxation.

Quantification of the total gel content in NR

The total gel content (microgel and macrogel) was estimated as the insoluble phase after dissolution of NR in cyclohexane.²⁶

RESULTS AND DISCUSSION

The effect of high-temperature mastication on the macrostructure and mesostructure of the model NR grades were evaluated in terms of their Mooney viscosity: MS3+4@100°C (Fig. 3) and total gel content, respectively (Fig. 4). The Mooney viscosity of grade TSR 10 samples, although initially higher at about 60 Mooney units, reduced much more rapidly and continuously throughout to less than 25 Mooney units after prolonged mastication for 13 min. Samples of grade TSR3CV meanwhile decreased slightly and seemed to attain a minima after just out 4 min of mastication. The differences in degradation rates could be linked to differences in chain entanglements, average molar masses, and molar mass distributions.^{12,17,23} Some differences were observed with respect to the degradation of the total gel contents

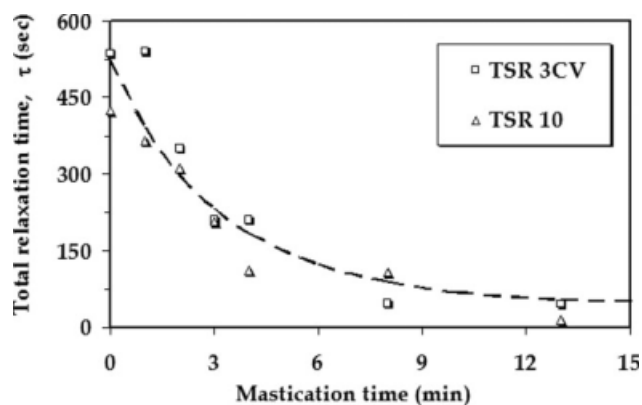


Figure 4 Effect of high-temperature internal mixer mastication on the total gel content of technically specified natural rubber of grades TSR10 and TSR3CV.

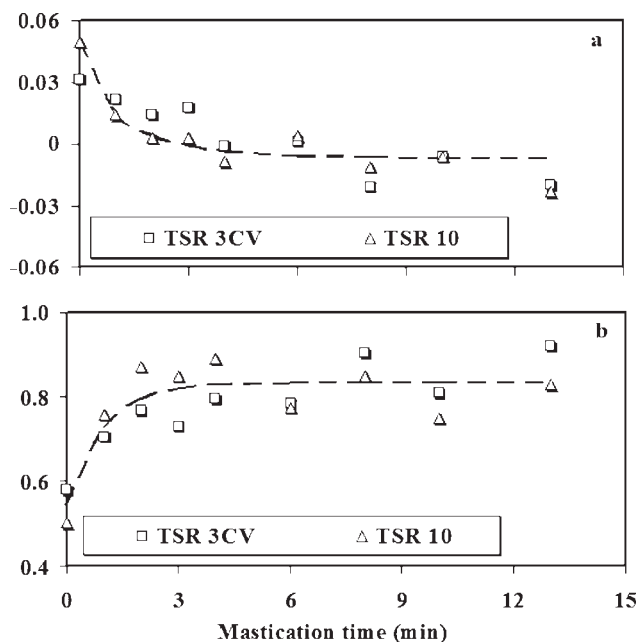


Figure 5 Effect of high-temperature internal mixer mastication on the nonlinear regression coefficients (a and b) obtained by modeling Mooney relaxation data with the Wu-Abbott model.

(macrogel and microgel) for the two rubber grades as mastication progressed (Fig. 4). This decrease was rather linear throughout for the TSR10 and different for the TSR3CV. For the TSR3CV, the total gel content seemed to get to a minimum value after ~ 6 min of mastication.

On using the regression coefficients generated from modeling the relaxation data to characterize the effects of high temperature mastication, the evolution of the macrostructure and mesostructure of the rubber grades were rather different. With the Wu-Abbott model [eq. (2)], high-temperature mastication had opposite effects on the regression coefficients (a and b) obtained. This model showed no discrimination among the rubber grades as the coefficients seemed to evolve similarly for the both grades (Fig. 5). The coefficient characterizing the elastic component of the material's viscoelasticity (a) reduced more rapidly at the onset of mastication to attain a minimum value after about 4 min of mastication, whereas the parameter that characterizes the viscous component (b) increased more rapidly at the onset of mastication to attain a maximum after a similar duration of mastication.

The terminal relaxation time (τ) from the Maxwell's triexponential model [eq. (2)] also seemed to characterize the effect of mastication on NR but in the same manner for the both rubber grades tested (Fig. 6). For the both rubber grades (TSR10 and TSR3CV), τ values decreased progressively from onset of mastication to attain a minimum after about

13 min. The continuous drop in τ could be associated with progressive reductions in the proportion of long polyisoprene chains, gel, or branching as mastication progresses. The evolution of τ was quite similar to that of the coefficient characterizing the elastic component of the material's viscoelasticity (a) from the Wu-Abbott model. However, whereas the value of a reduced more rapidly at the onset of mastication to attain a minimum value after about 4 min of mastication, that of τ reduced gradually but progressively and only seemed to approach a minimum on prolonged mastication. Although the two grades of NR (TSR10 and TSR3CV) were so different with respect to their initial molar mass distributions (Fig. 1; conducted on the cyclohexane-soluble fraction) and their inherent levels of the highly crosslinked cyclohexane-insoluble gel phase, the masticated rubbers showed similar responses for the mechanical models before and after mastication. These results could therefore indicate that although the relaxation of raw NR depends much on the molar mass of the polyisoprene chains and more on the total gel content,²⁷ high temperature mastication decomposes to a similar extent these components that account for the viscoelasticity of the raw elastomer. This could be confirmed by the rather loose fit between total relaxation time (τ) and total gel content (Fig. 7).

On using the Power law [eq. (3)] to model Mooney relaxation data, two coefficients were obtained, notably the power law constant for Mooney relaxation (a) and the power law index (b). The power law constant a represents the Mooney torque at 1 s after shearing stops and so should, in principle, be closely related to the normalized Mooney viscosity (Fig. 8 insert; $R^2 = 0.78$) and any deviations could be attributed to the effect of mastication on the instantaneous relaxation when shearing ceases. Although the effect of high-temperature

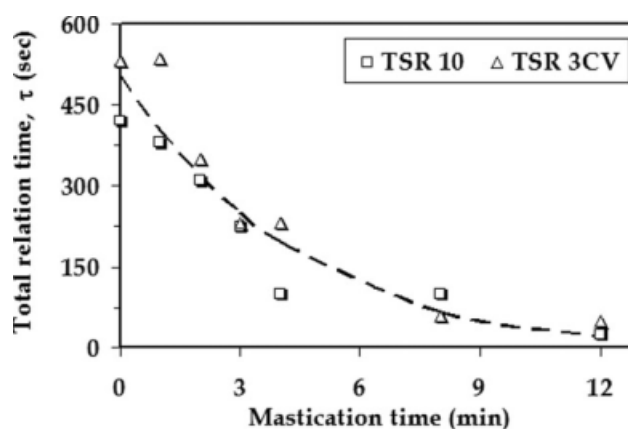


Figure 6 Effect of high-temperature internal mixer mastication on the terminal relaxation time (τ) obtained by modeling Mooney relaxation data with the Maxwell's triexponential equation.

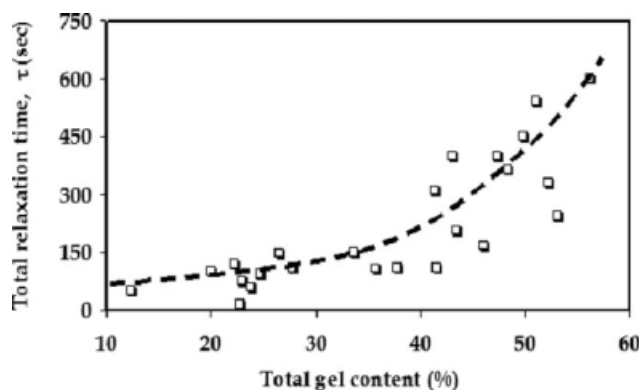


Figure 7 Relations between the terminal relaxation time (τ) and the total gel content of masticated and nonmasticated raw natural rubber.

mastication on the Mooney relaxation evaluated with the power law constant seems to show a trend (Fig. 8), the parameter lacked precision and relevance as the scatter of the Mooney torque relaxation was too erratic at times less than 1 s and the time was too short for any meaningful data to be collected.

When used to characterize the processability of elastomers, the value of the power law index is indicative of whether a fluid is Newtonian in nature ($b = 1$), shear thinning ($b < 1$), or shear thickening ($b > 1$).²⁸ In the framework of this study, the power-law index characterized the effect of high-temperature mastication on the Mooney relaxation of both NR grades in a similar manner (Fig. 9), increasing slightly from a mean of ~ 0.25 to attain a maximum after 3 min of mastication, and then reducing progressively with further mastication. The initial increase in the value of b on the onset of mastication could be associated with stress offshoot,²⁹ a phenomenon generally attributed to the instantaneous disen-

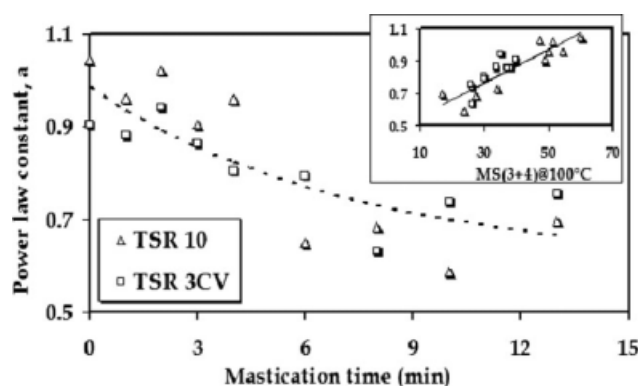


Figure 8 Effect of high-temperature internal mixer mastication on the power law constant (a) obtained by modeling Mooney relaxation data with the Power law model. Insert is the relationship between “ a ” and the Mooney viscosity.

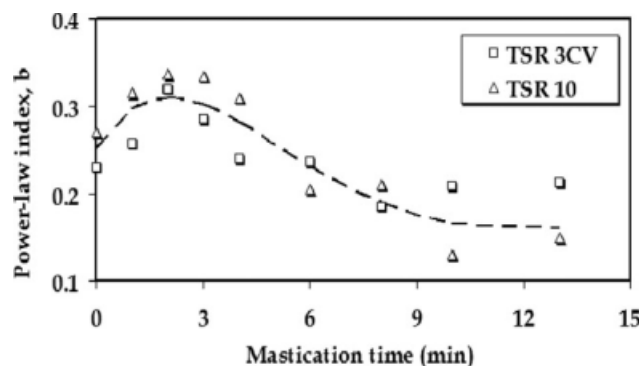


Figure 9 Effect of high-temperature internal mixer mastication on the power law index (b) obtained by modeling Mooney relaxation data with the Power law model.

tanglement of polyisoprene chains when shearing starts. However, after the peak value has been attained, the subsequent decrease in b could be associated with the progressive orientation/alignment of polymer chains, hence, loss of elasticity. The decrease in b on prolonged mastication indicates that the material becomes less elastic as mastication progressed. However, NR is predominantly shear thinning in nature ($b < 1$) and remained so throughout the mastication process.

CONCLUSIONS

Grades TSR10 and TSR3CV NR samples were masticated in air at high temperatures ($>115^{\circ}\text{C}$) and their processability assessed by using regression coefficients generated after modeling Mooney relaxation data using some mechanical models. Some of the coefficients generated appeared appropriate for characterizing the effect of high temperature mastication on NR's processability. The rapid and continuous drop in the magnitude of some coefficients with mastication could have been associated with a progressive breakdown of the polymer's matrix while their stagnation after a critical duration of mastication could be due to a balance between the proportions of long and short chains in the rubber matrix. Although the initial molar mass distributions of the two grades of NR, their evolution during mastication, and the inherent total gel contents were quite different, the responses of the both rubber grades evolved similarly throughout mastication, irrespective of the mechanical models tested, indicating therefore that mastication-induced breakdown affects to a similar extent the components responsible for the viscoelastic behavior of raw NR.

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